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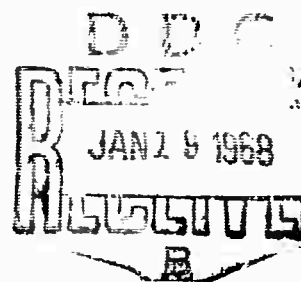
COLLISION-INDUCED ABSORPTION IN DIATOMIC MOLECULE/RARE-GAS MIXTURES

H. T. Yura

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PREFACE

This analysis was conducted for the Advanced Research Projects Agency as part of RAND's continuing study of the propagation of laser beams through the atmosphere. It examines in detail the characteristics of the collision-induced absorption of infrared and far-infrared radiation by symmetrical diatomic molecules and rare-gas atoms in order to provide a broader basis for the theoretical understanding of collision-induced absorption, which is an important factor limiting transmission in some atmospheric spectral windows. It is believed that the results reported here represent substantial progress toward that end.

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SUMMARY

A quantum mechanical calculation of collision-induced absorption
in the infrared and far-infrared spectral regions for mixtures consisting
of symmetrical diatomic molecules and rare-gas atoms is given. The induced
moment consists of a short-range overlap term and a long-range quadrupole
te: Near molecular transition lines the quadrupole term gives the
main contribution to the absorption, while in the far wings the overlap
term is dominant. The H_2-He, H_2-Ar and N_2-Ar systems are considered
and an estimate for the absorption coefficient near 10μ for N_2-N_2
systems is given.

ACKNOWLEDGMENTS

I would like to express my gratitude to H. A. Ory for suggesting the problem and Mrs. M. Lakatos for her endless patience in performing the numerical calculations.

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I. INTRODUCTION

The purpose of this Memorandum is to calculate the binary absorption coefficient of infrared and far-infrared radiation in mixtures consisting of symmetrical diatomic molecules and rare-gas atoms. Atoms and molecules with no permanent dipole moment, and consequently no dipole absorption coefficient proportional to the density, are considered. The absorption mechanism considered here is that due to the dipole moment induced between a pair of colliding atoms or molecules. For small-impact parameters the induced moment arises as a consequence of the distortion of the electron cloud during the collision of two particles, atoms, or molecules, while for larger-impact parameters the induced moment arises from the polarization of one particle by the quadrupole field of the other. The induced dipole moment is expected to be nonzero when the colliding pair are within a few molecular radii of each other. Thus, absorption takes place within the duration of a collision and the probability of absorption is proportional to the product of the densities of the two species.

Collision-induced absorption in rare-gas mixtures was discovered experimentally by Kiss and Welsh[1] and further studied by Bosomworth and Gush.[2] Recently, Levine and Birnbaum[3,4] have made a theoretical calculation of induced absorption in rare-gas mixtures using a simple model to describe the variation of the collision-induced dipole moment with internuclear separation. They obtain an analytic expression for the absorption spectrum which agrees well with the experiments. Previously, J. Van Kranendonk[5] has presented a theory for the integrated absorption coefficient in diatomic molecules. Interest here is in

the absorption coefficient as a function of the frequency of the incident radiation field and <u>not</u> in this function integrated over all frequencies.

The energy absorbed during a collision between two dissimilar rare-gas atoms goes into increasing the translational kinetic energy only. The effects on the induced absorption due to the rotational transitions that occur in the diatomic molecule are investigated here. The frequency of the applied radiation field is taken to be less than the frequency of the first excited vibrational level of the diatomic molecule (4159.4 cm^{-1} for H_2 and 2330.7 cm^{-1} for N_2; see Ref. 6); consequently, vibrational effects on the absorption need not be considered. The absorbed energy in this case goes into both rotational and translational energy.

In Section II a formal expression for the absorption coefficient is written and the phenomenological induced dipole moment is introduced and discussed. In Section III an analytic expression for the absorption coefficient is derived, and in Section IV an estimate is made of the parameters for H_2-rare atom, N_2-rare atom, and N_2-N_2 collisions, and numerical values of the absorption coefficient are given as calculated as a function of frequency for these cases.

These calculations are aimed at providing a broader basis for the theoretical understanding of collision-induced absorption, which is an important factor limiting transmission in some atmospheric spectral windows. For example, collision-induced absorption in O_2 is dominant at the Nd laser wavelength of 1.06μ, and collision-induced absorption in the far wings of H_2O lines is important at the CO_2 laser wavelength of 10.6μ. These absorptions involve more complicated mechanisms and require further development for their treatment.

II. FORMAL EXPRESSION FOR THE INDUCED ABSORPTION COEFFICIENT

Gaussian units are used with $\hbar = c = 1$; then $e^2 \cong 1/137$. The absorption coefficient $\alpha = (2\pi/c)\Gamma$, where Γ is the transition rate. That is,

$$\alpha(\omega) = \frac{(2\pi)^2}{V}\left\langle \sum_f \omega |(\vec{\mu} \cdot \vec{e})_{if}|^2 (P_i - P_f)\, \delta(\omega_{fi} - \omega) \right\rangle_i \qquad (1)$$

In Eq. (1), V is the volume of the sample, $\vec{\mu}$ is the induced dipole moment of the system of particles, $\vec{e}$ is the unit polarization vector of the incident radiation field of frequency ω, $\omega_{fi} = E_f - E_i$ is the energy difference between a final state f and an initial state i of the molecular system respectively. P_i and P_f are the statistical weights of the initial and final particle states.[*] Also, Eq. (1) indicates a sum over final states (denoted by $\sum_f$) and an average over initial states (denoted by $\left\langle \ \right\rangle_i$). The appearance of the factor $(P_i - P_f)$ takes into account both absorption (the P_i term) and the reverse process, spontaneous emission (the P_f term). It is assumed throughout that the temperature T of the system is so low that all of the particles may be taken to be in their electronic ground states.

Consider a system of rare-gas atoms (density n_1) and symmetrical diatomic molecules (density n_2). The dipole moment arises from binary collisions between atoms and molecules and between molecules.[**] Consider first the term in α proportional to $n_1 n_2$, that is, absorption

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[*] Explicit expressions for P_i and P_f are given in Eq. (7) below.

[**] There can be no net induced dipole moment for two identical rare-gas atoms (in the same electronic state) since the system is completely symmetrical about the center of mass. However, this is not the case for two diatomic molecules.

by the induced moments arising from the collision of a rare-gas atom and a symmetrical diatomic molecule. Later on, the term proportional to n_2^2 (i.e., absorption arising from binary molecular collisions) is estimated.[*] It is assumed that

$$\vec{\mu}(\vec{R}_1,\ldots,\vec{R}_N) = \sum_{i=1}^{Vn_1} \sum_{j=2}^{Vn_2} \vec{\mu}(R_{ij}) \qquad (2)$$

i.e., the dipole moment arises from binary collisions and is a function of the distance between the centers of mass (R_{ij}) of the two colliding particles. The wave functions describing the centers of mass motion of the particles can, in the first approximation, be taken as plane waves. Then by a straightforward procedure Eq. (1) may be reduced to a form expressing α in terms of two-particle matrix elements.[4] Thus

$$\alpha = 4\pi^2 \, n_1 \, _2\omega \left\langle \sum_f |(\vec{\mu}(R)\cdot\vec{e})_{if}|^2 \, (P_i-P_f) \, \delta(\omega_{fi}-\omega) \right\rangle_i \qquad (3)$$

where now the initial and final states refer to the two-particle system interacting with the radiation field,

$$|\vec{\mu}(R)\cdot\vec{e}|_{if} = \int d^3R \, \varphi_f(R)^* (\vec{\mu}(R)\cdot\vec{e})\varphi_i(R) \qquad (4)$$

where

$$\left.\begin{array}{l} \varphi_i(R) = e^{i\vec{k}\cdot\vec{R}} u_k(R) \, \psi_{J_i}(\Omega) \cong e^{i\vec{k}\cdot\vec{R}} \, \psi_{J_i}(\Omega) \\[3mm] \varphi(R) = e^{i\vec{k}'\cdot\vec{R}} u_{k'}(R) \, \psi_{J_f}(\Omega) \cong e^{i\vec{k}'\cdot\vec{R}} \, \psi_{J_f}(\Omega) \end{array}\right\} \qquad (5)[**]$$

---

[*] Experimentally these two cases may be distinguished by (or example) arranging $n_1 \gg n_2$ so that the absorption arises predominately from collisions between diatomic molecules and rare-gas atoms.

[**] The $\mu(R)$ term in the relative two-particle wave function, which is determined by solving the Schoedinger equation with the two-particle interaction, is taken to be unity in the first approximation. This corresponds to taking straight line collision paths in the classical approach.[3,4]

ψ_J are the rotational wave functions and k and k' are the relative momenta of the colliding particles before and after the collision, respectively.

For the atom-molecule system,

$$\left.\begin{aligned}
E_i &= k^2/2m + E_{J_i} \\[1em]
E_f &= k'^2/2m + E_{J_f} \\[1em]
m &= \text{reduced mass} = m_1 m_2/(m_1 + m_2) \\[1em]
E_J &= \text{rotational energy} = BJ(J+1)
\end{aligned}\right\} \qquad (6)$$

where J is the rotational quantum number and B is the rotational constant of the molecule. The statistical weights of the initial and final particle states are given by

and

$$\left.\begin{aligned}
P_i &= (2J_i+1)g_i \, e^{-E_i/\varkappa T} \, (1/2\pi m \varkappa T)^{3/2} \\[1em]
P_f &= (2J_f+1)g_f \, e^{-E_f/\varkappa T} \, (1/2\pi m \varkappa T)^{3/2}
\end{aligned}\right\} \qquad (7)$$

where $\varkappa$ is the Boltzmann constant, and g_i and g_f are the statistical weights for the nuclear spin states of the diatomic molecule. It is well known that the relative statistical weights for the symmetric and anti-symmetric spin states are[6]

$$\left.\begin{aligned}
g_{(sym)}/g_{(antisym)} &= (I+1)/I \text{ for I integral} \\[1em]
&= I/I+1 \text{ for I half-integral}
\end{aligned}\right\} \qquad (8)$$

where I is the nuclear spin. Upon combining Eqs. (3)-(8),

$$\alpha(\omega) = 4\pi^2 n_1 n_2 \omega (1/2\pi m\kappa T)^{3/2}(2J_i+1)^{-1} \sum_{J_i,J_f,M_i,M_f} \int \frac{d^3k}{(2\pi)^3} \int \frac{d^3k'}{(2\pi)^3}$$

$$\times \left|(\vec{\mu}\cdot\vec{e})_{k'J_f,kJ_i}\right|^2 \frac{e^{-(k^2/2m\kappa T)}}{\sum\limits_i (2J_i+1)g_i \; e^{-\frac{B}{\kappa T}J_i(J_i+1)}} \left\{(2J_i+1)g_i \right. \tag{9}$$

$$\left. - (2J_f+1)g_f e^{-\omega\kappa T}\right\} e^{-\frac{B}{\kappa T}J_i(J_i+1)} \delta(\omega_{fi}-\omega)$$

where

$$\omega - \omega_{fi} = \omega - \frac{1}{2m}(k'^2-k^2) - E_{J_f J_i} \tag{10}$$

and

$$E_{J_f J_i} = E_{J_f} - E_{J_i} \tag{11}$$

In Eq. (9) the summations over the initial and final continuum states k and k' have been replaced by integrations over d^3k and d^3k' respectively.

To proceed, an analytic form is specified for the induced dipole moment. The induced dipole moment of a pair of colliding particles may be resolved into two parts. One part is the overlap dipole moment which results from the distortion of the electron cloud during close collisions ($r \lesssim$ collision diameter). The other part of the induced dipole moment arises from the polarization of one particle by the quadrupole field of the other and vice versa. The quadrupole-induced dipole moment arises from long-range collision ($r \gtrsim$ collision diameter). These two parts of the moment are discussed separately.

In view of the close agreement of Levine and Birnbaum's[3,4] theory with the experimental results, we use the same functional form for the overlap-induced dipole moment between the rare-gas atom and each nucleus of the diatomic molecule. The form they use is $\mu(r) = \mu_c \gamma r \exp(-\gamma^2 r^2)$, where γ^{-1} and μ_c are the range and strength respectively of the dipole moment. In the cases considered here $\gamma \sim (1-2) \, \overset{o}{A}^{-1}$. That is, the important values of r are of the order of the internuclear separation of the molecule. For distance in this range the rare-gas atom "sees" each nucleus separately. This, however, would not be the case when γ^{-1} is much larger than the internuclear separation.

In the present calculation any interparticle potential is ignored, and hence straight line collision paths are assumed. Realistically, a potential exists between the particles which contains a repulsive part that prevents the two particles from approaching too close to one another, so there is actually a small moment for distances within the range of the repulsive part of the interparticle potential. The factor (γr) in the moment cuts off the moment for $r \lesssim \gamma^{-1}$. Similarly, for large interparticle separation, when the electron clouds do not overlap there is very little contribution to the overlap moment. The factor $\exp(-\gamma^2 r^2)$ cuts off the moment for $r \gtrsim \gamma^{-1}$. Strictly speaking the repulsive and overlap ranges are not equal. In this calculation, as in Refs. 3 and 4, a single range is used to specify the induced moment.

By using the modified gaussian model for the induced overlap moment Levine and Birnbaum were able to obtain a simple analytic expression for the absorption spectrum. By matching the theoretical and experimental results (for He-Ne, He-Ar and Ne-Ar systems) at the

peak of the spectrum they obtained values of γ and μ_o. Using these
values of γ and μ_o they obtained good agreement over nearly the entire
range of the spectrum (especially for He-Ar systems). For the cases
considered here, H_2 and N_2/rare-gas atom absorption, no experimental
results exist as yet. However, using the mathematical form for the
moment that was used by Levine and Birnbaum leads to analytic expres-
sions for the absorption spectrum in terms of μ_o and γ. Then physical
arguments are used to estimate values for μ_o and γ in terms of the
values obtained by Levine and Birnbaum for the rare-gas cases. In
view of their good agreement with the experimental results this
procedure seems justifiable.

The main contribution to the induced dipole moment arises for
values of r where $r\gamma \sim 1$. In the cases considered here, $\gamma \sim (1-2)\overset{o}{A}^{-1}$.
That is, the important values of r are of the order of the size of
the atom or molecule (the electron clouds overlap and hence distort
the charge distribution).

The quadrupole-induced dipole moment is equal to the quadrupole
field of particle one at the position of particle two times the
polarizability of particle two, and vice versa. In the case of a
diatomic molecule/rare-gas atom collision there is only one term,
since rare-gas atoms possess no quadrupole moment. Qualitatively
the overlap-induced moment contributes to the high-frequency part of
the absorption spectrum, since the overlap moment arises from close
collision. On the other hand the quadrupole-induced moment contributes
to low frequencies in the Q and O branches and frequencies near the
rotational transitions in the S branches, since the quadrupole-induced

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moment is due to distant collisions. (Near the rotational transition frequencies the momentum transfer is small.)

III. CALCULATION OF THE ABSORPTION SPECTRUM

OVERLAP-INDUCED DIPOLE MOMENT

The induced dipole moment between a colliding rare-gas atom and a symmetrical diatomic molecule is taken as a superposition of the atom interacting with each of the two atomic components of the molecule respectively. That is,

$$\vec{\mu}^{(o)}(r) = \vec{\mu}^{(o)}(r_1) + \vec{\mu}^{(o)}(r_2) \tag{12}$$

where r_1 and r_2 are the separations of the atom from each of the two nuclei respectively. Choosing a coordinate system with the z-axis parallel to the polarization vector of the incident radiation field and calling the molecular internuclear separation vector $2\vec{a}$ gives

$$\vec{\mu}^{(o)}(r)\cdot\vec{e} = \mu_o \gamma \left[(r_1)_z\ e^{-\gamma^2 r_1^2} + (r_2)_z\ e^{-\gamma^2 r_2^2} \right] \tag{13}$$

where

$$\vec{r}_1 = \vec{r} - \vec{a} \quad \text{and} \quad \vec{r}_2 = \vec{r} + \vec{a}$$

First the matrix element of $\vec{u}\cdot\vec{e}$ between the initial and final continuum states is calculated. Suppressing the rotational quantum numbers for brevity, we have

$$(\vec{\mu}^{(o)}\cdot\vec{e})_{k'k} = \int d^3 r\ e^{-i\vec{k}'\cdot\vec{r}}(\vec{\mu}\cdot\vec{e})\ e^{i\vec{k}\cdot\vec{r}}$$

$$= \int d^3 r\ (\vec{\mu}\cdot\vec{e})\ e^{-i\vec{Q}\cdot\vec{r}} \tag{14}$$

where

$$\vec{Q} = \vec{k}' - \vec{k}$$

Substituting Eq. (13) into Eq. (14) gives

$$(\vec{\mu}^{o} \cdot \vec{e})_{k'k} = (\mu_z)_{k'k} = \gamma\mu_o\left\{ e^{i\vec{Q}\cdot\vec{a}} \int d^3r_1 e^{i\vec{Q}\cdot\vec{r}_1} z_1 e^{-\gamma^2 r_1^2} \right.$$

$$\left. + e^{-iQ\cdot a} \int d^3r_2 e^{i\vec{Q}\cdot\vec{r}_2} z_2 e^{-\gamma^2 r_2^2} \right\}$$

$$= \gamma\mu_o e^{i\vec{Q}\cdot\vec{a}} \int d^3r \; z \; e^{i\vec{Q}\cdot\vec{r}} e^{-\gamma^2 r^2} + \text{terms } \vec{a} \to -\vec{a} \quad (15)$$

The integral appearing in Eq. (15) is elementary and easily found to be:[*]

$$\int d^3r \; z \; e^{i\vec{Q}\cdot\vec{r}} e^{-\gamma^2 r^2} = \frac{\pi^{3/2}}{2i} \gamma^{-5} Q_z e^{-(Q^2/4\gamma^2)}$$

Substituting this value into Eq. (15) gives

$$(\vec{\mu}^{o} \cdot \vec{e})_{k'k} = \frac{\mu_o \pi^{3/2}}{2i} \gamma^{-4} (\vec{Q} \cdot \vec{e})_z e^{i\vec{Q}\cdot\vec{a}} e^{-(Q^2/4\gamma^2)}$$

$$\text{(16)}$$

$$+ \text{ terms } \vec{a} \to -\vec{a}$$

Next one must calculate the matrix element of Eq. (16) between initial and final rotational states of the molecule. Suppressing the subscripts k' and k,

$$(\mu_z^o)_{J_f M_f, J_i M_i} \equiv \left\langle J_f M_f | \mu_z | J_i M_i \right\rangle$$

where the initial and final rotational states are referred to the z-axis. Suppressing, for brevity, terms that do not depend on angular coordinates,

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[*] Due to the rapid convergence of the integrand for $r \gg \gamma^{-1}$ negligible error is introduced upon extending the upper limit of the r integration to $+\infty$.

we find

$$\left\langle J_f M_f \middle| \mu_z^o \middle| J_i M_i \right\rangle = \left\langle J_f M_f \middle| Q_z \, e^{i\vec{Q}\cdot\vec{a}} \middle| J_i M_i \right\rangle + \text{terms } \vec{a} \rightarrow -\vec{a} \qquad (17)$$

For frequencies of the order of the peak in the absorption spectrum, $|Qa| \lesssim 1$ and hence one may expand $e^{i\vec{Q}\cdot\vec{a}}$ and retain the first nonvanishing term. In the case of diatomic molecule/rare-gas atom collisions the main contribution comes from setting $e^{i\vec{Q}\cdot\vec{a}} \simeq 1$. That is, for diatomic molecule/rare-gas atom collisions the overlap-induced moment is independent of the orientation of the molecule. On the other hand, for molecular-molecular collisions involving identical molecules (in the ground electronic and vibrational states) the matrix elements of the angle-independent part of the overlap-induced moment are zero, since the colliding system possesses a center of symmetry. Hence, the lowest-order nonvanishing term for systems such as N_2-N_2, H_2-H_2 comes from the $(Q \cdot a)^2$ term in the expansion of $e^{i\vec{Q}\cdot\vec{a}}$ (see Eq. (17)). The angle-dependent part of the overlap moment is small,[7] and hence for frequencies of the order of the peak the overlap moment contributes to the Q branch only. For frequencies such that $|Qa| \gtrsim 1$ (tail of the spectrum), a power series expansion of $e^{i\vec{Q}\cdot\vec{a}}$ is not valid and the overlap moment is strongly angle-dependent. For example, in N_2-N_2 absorption the peak in the spectrum is approximately 100 cm^{-1} and arises from quadrupole-induced dipole moments. Near 1000 cm^{-1} ($\sim CO_2$ laser wave number) where $Qa > 1$, the main contribution to the absorption is expected to come from the angle-dependent terms in the overlap-induced moment. For the present, attention is focused on diatomic molecule/rare-gas atom collisions near the peak of the spectrum. Later on, the absorption in N_2-N_2 collisions near the CO_2 laser wavelength is estimated.

Setting $e^{i\vec{Q}\cdot\vec{a}} \simeq 1$ in Eq. (16), the overlap matrix element is given by

$$(\vec{e}\cdot\vec{\mu}^o)_{k'k} = -i\mu_o\pi^{3/2}\gamma^{-4}(\vec{Q}\cdot\vec{e})e^{-(Q^2/4\gamma^2)}\delta_{J_fJ_i}\delta_{M_fM_i} \qquad (18)$$

QUADRUPOLE-INDUCED DIPOLE MOMENT

For diatomic molecule/rare-gas atom systems the long range quadrupole-induced moment $\vec{\mu}^{(q)}$, which can be inferred from Ref. 7, is given by

$$\vec{e}\cdot\vec{\mu}^{(q)} = \frac{3q_o\alpha_o}{r^4}\left(\frac{4\pi}{5}\right)\left[\sum_{m=-2}^{m=+2} Y_{2m}(\Omega_a) Y_{2m}(\Omega_r)\right]\vec{e}\cdot\vec{e}_r \quad \text{for } r \gtrsim \sigma \qquad (19)$$

where the z-axis is taken parallel to $\vec{e}$, $\vec{e}_r$ is a unit vector in the r-direction, Ω_a and Ω_r are the angular coordinates of $\vec{r}$ and $\vec{a}$ respectively, α_o is the polarizability of the rare-gas atom, and q_o is the quadrupole moment of the diatomic molecule. The assumption is made that the quadrupole-induced moment has meaning only for values of $r \gtrsim \sigma$, which is the collision diameter of the colliding particles.

Upon taking matrix elements of Eq. (19) between initial and final continuum states,

$$(\vec{e}\cdot\vec{\mu}^{(q)})_{k'k} = \frac{12\pi}{5}\alpha_o q_o\, Y_{20}(\Omega_a)\, \vec{e}\cdot\vec{I} \qquad (20)$$

where

$$\vec{I} = \int \vec{e}_r\, Y_{20}(\Omega)\, e^{i\vec{Q}\cdot\vec{r}}\, \frac{d^3r}{r^4} \qquad (21)$$

and $\vec{Q} = \vec{k}'-\vec{k}$. $\vec{I}$ is a vector and must be proportional to $\vec{Q}$. That is, $\vec{I}=I\vec{Q}$ where $I=(\vec{Q}\cdot\vec{I})/Q^2$. Then

$$\vec{Q}\cdot\vec{I} = \int \vec{Q}\cdot\vec{e}_r\, Y_{20}(\Omega)\, e^{i\vec{Q}\cdot\vec{r}}\, \frac{d^3r}{r^4}$$

Taking the z-axis of integration along $\vec{Q}$ and expanding $e^{i\vec{Q}\cdot\vec{r}}$ in terms of spherical harmonics,

$$\vec{Q}\cdot\vec{I} = i\sqrt{20\pi}\ Q \int_\sigma^\infty \frac{dr}{r^3} \frac{\partial j_2(Qr)}{\partial Q} \tag{22}$$

where j_2 is the spherical Bessel function of second order. The lower limit on the r integration has been set equal to the collision diameter σ appearing in the interparticle potential.

Strictly speaking, setting the lower limit arbitrarily equal to σ is incorrect. Upon introducing the two-particle distribution function into the integrand of Eq. (22), one can now integrate over all r. The two-particle distribution function, in the low density limit and at temperatures considered here, is proportional to $e^{-V(r)/\kappa T}$ where $V(r)$ is the interparticle potential. Any realistic interparticle potential (for example the Lennard-Jones potential) becomes very large for small r ($r \ll$ size of molecule), and hence $(e^{-V(r)/\kappa T} \ll 1)$, a negligible contribution to the integral, comes from small r. For $r \gtrsim$ size of the molecule, $V(r) \sim 0$ (i.e., the two-particle distribution function is constant). The main contribution to the integral comes from $r \simeq \sigma$. In view of other approximations involved in the calculation it is felt that unnecessary mathematical complexity is introduced by using the exact two-particle distribution function. Therefore we use, as an approximation, a distribution which is zero for $r < \sigma$ and is equal to unity for $r \geq \sigma$.

For frequencies $\omega \lesssim \kappa T$ for the Q branch, and frequencies near the rotational transition frequencies for the S branch, Q, the momentum transfer, $\sim\sqrt{2m\kappa T}$. For κT approximately equal to room temperature and

values of m and σ considered here, $Q\sigma \gg 1$ and hence the asymptotic
value of j_2 may be used. Setting $x = Qr$, Eq. (22) becomes

$$\vec{Q}\cdot\vec{I} = \sqrt{20\pi} \ i \ Q^2 \int_{Qc}^{\infty} \frac{d[j_2(x)]}{x^2}$$

$$\cong \sqrt{20\pi} \ i \ Q^2 \ \frac{\sin Q\sigma}{(Q\sigma)^3} + 0(Q\sigma)^{-4} + \cdots \qquad (23)$$

Therefore,

$$\vec{I}\cdot\vec{e} = (\vec{Q}\cdot\vec{e})(\vec{Q}\cdot\vec{I})/Q^2$$

$$\cong \sqrt{20\pi} \ i(\vec{Q}\cdot\vec{e})\frac{\sin Q\sigma}{(Q\sigma)^3}$$

Thus

$$(\vec{e}\cdot\mu^{(q)})_{k'k} = \frac{3}{\sqrt{5}} \ \alpha_o q_o (4\pi)^{3/2}(\vec{Q}\cdot\vec{e}) \ \frac{\sin Q\sigma}{(Q\sigma)^3} \ Y_{20}(\Omega_a) \qquad (24)$$

Taking matrix elements with respect to the rotational wave functions
(suppressing factors that do not depend on rotational quantum numbers),
it is found that

$$\left\langle J_f M_f \left| \vec{e}\cdot\vec{\mu}^{(q)} \right| J_i M_i \right\rangle \sim \left\langle J_f M_f \left| Y_{20} \right| J_i M_i \right\rangle$$

$$= \left[\frac{5(2J_i+1)}{4\pi(2J_f+1)}\right]^{\frac{1}{2}} C(J_i 2 J_f, M_i 0) C(J_i 2 J_f, 00) \qquad (25)$$

where the C's are the well-known Clebsch-Gordan coefficients.[3] From
Eq. (25) the selection rules for quadrupole absorption are easily
obtained; they are $\Delta J = (J_f - J_i) = 0, \pm 2$ and $\Delta M_i = 0$. From Eqs. (24)
and (25) it is found that

$$\left\langle J_f M_f \left| (\vec{e}\cdot\vec{\mu}^{(q)})_{k'k} \right| J_i M_i \right\rangle = 12\pi i \alpha_o q_o (\vec{Q}\cdot\vec{e}) \frac{\sin Q\sigma}{(Q\sigma)^3}\left(\frac{2J_i+1}{2J_f+1}\right)^{\frac{1}{2}}$$

$$\times \ C(J_i 2J_f, M_i 0)C(J_i 2J_f, 00) \qquad (26)$$

where $\vec{Q} = \vec{k}' - \vec{k}$.

CALCULATION OF THE ABSORPTION SPECTRUM

According to Eq. (9), it is necessary to square the matrix elements of $U \equiv \vec{\mu}\cdot\vec{e}$ ($\vec{\mu} = \vec{\mu}^0 + \vec{\mu}^{(q)}$) and then sum over final states (rotational and continuum) and average over initial states (rotational and continuum). Consider the rotational part first: suppressing notation that does not depend on rotational quantum numbers, the average for a given initial rotational state takes the form

$$\overline{U^2} \equiv (2J_i+1)^{-1} \sum_{M_i, M_f} \left| \left\langle J_f M_f \left| \vec{\mu}\cdot\vec{e} \right| J_i M_i \right\rangle \right|^2$$

where $\vec{\mu}\cdot\vec{e} = (\vec{\mu}^{(0)} + \vec{\mu}^{(q)})\cdot\vec{e}$. From Eqs. (18) and (26) it is found that

$$\overline{U^2} = (\vec{Q}\cdot\vec{e})^2 \left\{ A_o^2\, e^{-(Q^2/2\gamma^2)}\delta_{J_f J_i} + A_q^2(i,f)\frac{\sin^2 Q\sigma}{(Q\sigma)^6} \right\}$$

$$= (\vec{Q}\cdot\vec{e})^2 \ (R_o + R_q) \qquad (27)^*$$

where

$$A_o = \mu_o\, \pi^{-3/2}\gamma^{-4}$$

and

$$A_q^2(i,f) = (12\pi\alpha_o q_o)^2 \left(\frac{1}{2J_f+1}\right) C^2(J_i 2J_f, 00)$$

___

*No cross term between overlap and quadrupole moment appears in Eq. (27). The cross term is proportional to

$$\sum_{M_i, M_f} C(J_i 2J_f, M_i 0)\delta_{J_i J_f} = \sum_{M_i} C(J_i 2J_i, M_i 0) = 0$$

The first te n in Eq. (27) is the contribution from the overlap term, while the second is the contribution from the quadrupole term. The angle-independent overlap term contributes to the Q branches only, while the quadrupole term contributes to the S, Q and 0 branches.

To evaluate the integrals over $\vec{k}$ and $\vec{k}'$ indicated in Eq. (9), variables are changed from $\vec{k}$, $\vec{k}'$ to $\vec{k}$, $\vec{Q}$ respectively. Then (suppressing factors that do not depend on k or Q),

$$\alpha(\omega) \sim \int \frac{d^3Q}{(2\pi)^3} \int \frac{d^3k}{(2\pi)^3} e^{-\varepsilon k^2} \overline{U^2} \delta\left[(2m)^{-1}(Q^2+2\vec{Q}\cdot\vec{k}-\Delta^2)\right] \qquad (28)$$

where

$$\Delta^2 = 2m(\omega - E_{J_f J_i})$$

and

$$\varepsilon = 1/2m\varkappa T$$

Holding $\vec{Q}$ fixed for the k integration,

$$\alpha(\omega) \sim (2\pi)^{-2}(m/Q) \int k \, dk \, d(\cos \chi) e^{-\varepsilon k^2} \delta(\cos \chi + \frac{Q^2 - \Delta^2}{2Qk})$$

where χ is the angle between $\vec{k}$ and $\vec{Q}$ and the $\vec{Q}$ integral is suppressed. Performing the integral over $\cos \chi$,

$$\alpha(\ ) \sim (2\pi)^{-2}(m/Q) \int_{k_Q}^{\infty} k \, dk \, e^{-\varepsilon k^2} \qquad (29)$$

where

$$k_Q = \left|\frac{\Delta^2 - Q^2}{2Q}\right|$$

The limits on the k integral are determined by requiring $|\cos \chi| \leq 1$ and $k \geq 0$. The integral appearing in Eq. (29) is elementary, and

$$\alpha(\omega) \sim (2\pi)^{-2}(m/2Q\varepsilon) e^{-\varepsilon k_Q^2}.$$

Hence from Eq. (28),

$$\alpha(\omega) \sim (2\pi)^{-5} (m/2\epsilon) \int \frac{d^3Q}{Q} e^{-\epsilon k_Q^2} (\vec{Q}\cdot\vec{e})^2 (R_o + R_q)$$

R_o and R_q are defined in Eq. (27). When the z-axis of integration is chosen to be parallel to $\vec{e}$, the angular integration becomes elementary and gives[*]

$$\alpha(\omega) \sim (2\pi)^{-4} (m/3\epsilon) \int_0^\infty Q^3 dQ e^{-\epsilon k_Q^2} (R_o + R_q)$$

$$= (2\pi)^{-4} (m/3\epsilon) e^{\epsilon\Delta^2/2} \int_0^\infty Q^3 dQ \left\{ A_o^2 e^{-[Q^2(\frac{1}{2\gamma^2} + \frac{\epsilon}{4}) + \frac{\epsilon\Delta^4}{4Q^2}]} \right.$$

$$\left. + A_q^2 \frac{\sin^2 Q\sigma}{(Q\sigma)^6} e^{-[\frac{\epsilon Q^2}{4} + \frac{\epsilon\Delta^4}{4Q^2}]} \right\} \qquad (30)$$

$$= (2\pi)^{-4} (m\Delta^4/3\epsilon) e^{\epsilon\Delta^2/2} \int_0^\infty x^3 dx \left\{ A_o^2 e^{-[x^2(a+b) + \frac{b}{x^2}]} \right.$$

$$\left. + \frac{A_q^2 \sin^2 Bx}{(Cx)^6} e^{-b(x^2 + \frac{1}{x^2})} \right\}$$

where $a = \Delta^2/2\gamma^2$, $b = \epsilon\Delta^2/4$, and $C = \Delta\sigma$. Two types of integrals appear in Eq. (30). The first is of the form

---

[*]Strictly speaking, the upper limit on the quadrupole term should be $Q_{max} \sim 2\pi/\sigma$. However, due to the rapid convergence of the integrand for large Q the upper limit has been set to ∞.

$$I_1 = \int_0^\infty x^3 \, dx \, e^{-(\alpha x^2 + \frac{\beta}{2})} = \tfrac{1}{2} \int_0^\infty y \, dy \, e^{-(\alpha y + \frac{\beta}{y})}$$

$$= \tfrac{1}{2} \frac{\partial^2}{\partial \alpha^2} \left\{ \int_0^\infty \frac{dy}{y} \, e^{-(\alpha y + \frac{\beta}{y})} \right\}$$

$$= \frac{\partial^2 K_0 (2\sqrt{\alpha\beta})}{\partial \alpha^2} \quad {}^*$$

$$= (\beta/\alpha) \, K_2 (2\sqrt{\alpha\beta})$$

where K_n is the modified Bessel function of the second kind of order n.

The second integral appearing in Eq. (30) cannot be expressed in closed form. However, the limiting cases of large and small C lead to closed form expressions.

$$I_2 = \int_0^\infty \frac{dx}{x^3} \, e^{-(\alpha x^2 + \frac{\beta}{x^2})} \sin^2 Cx$$

For $C \ll 1$ the $\sin^2$ term varies slowly over the region where the exponential term is nonzero. Applying the method of steepest descent to I_2 it is found that

$$I_2 \simeq (\alpha/\beta)^{\frac{1}{2}} \sin^2 [C(\beta/\alpha)^{\frac{1}{4}}] \, K_0 (2\sqrt{\alpha\beta}), \quad C \ll 1$$

$$\cong C^2 K_0 (2\sqrt{\alpha\beta})$$

For $C \gg 1$ the $\sin^2$ term oscillates rapidly over the region where the exponential term is nonzero, and hence its average value, $\tfrac{1}{2}$, may be substituted, yielding

---

*See Ref. 9.

$$I_2 \simeq \tfrac{1}{2} K_1(2 \sqrt{\alpha\beta}), \quad C \gg 1$$

The integrals appearing in Eq. (30) may be obtained by substituting $\alpha = a+b$, $\beta = b$ in I_1 and $\alpha = \beta = b$ in I_2. The result is

$$\alpha(\omega) \sim (2\pi)^{-4}(m\Delta^4/3\epsilon) \, e^{\epsilon\Delta^2/2} \left\{ \frac{A_o^2}{1+\delta} K_2(2b\sqrt{1+\delta}) + \frac{A_q^2}{c^6} I_q \right\} \qquad (31)$$

where

$$\delta = a/b = 4m\varkappa T/\gamma^2$$

and

$$I_q = \int_0^\infty \frac{dx}{x^3} e^{-(x^2 + \frac{1}{x^2})b} \sin^2 Cx$$

$$\to c^2 K_0(2b) \quad \text{for } C \ll 1$$

$$\to \tfrac{1}{2} K_1(2b) \quad \text{for } C \gg 1$$

Replacing all of the factors previously withheld, it is found that

$$\alpha(\omega) = \frac{n_1 n_2 m^3 \omega}{3\pi^3(2\pi m\varkappa T)^{\frac{1}{2}} Z} \sum_{J_i, J_f} \left\{ (\omega-E_{J_f J_i})^2 e^{\frac{(\omega-E_{J_f J_i})}{2\varkappa T}} g_i \left[(2J_i+1) \right. \right.$$

$$- (2J_f+1) e^{-\omega/\varkappa T} \left] e^{-\frac{B}{\varkappa T} J_i(J_i+1)} \left[\frac{A_o^2}{1+\delta} K_2(2b\sqrt{1+\delta}) \, \mathcal{E}_{J_i J_f} \right. \right.$$

$$\left. \left. \left. + \frac{A_q^2(i,f)}{c^6} I_q \right] \right\} \qquad (32)$$

where

$$b = (\omega - E_{J_f J_i})/4\kappa T$$

$$\delta = 4m\kappa T/\gamma^2$$

$$C = \Delta\sigma$$

$$Z = \sum_{J_i} (2J_i+1)g_i \, e^{-\frac{B}{\kappa T} J_i(J_i+1)}$$

A_o, A_q and I_q are given in Eqs. (27) and (31) respectively. In obtaining Eq. (32) g_f has been set equal to g_i, since the interaction does not change the nuclear spin.

Examining the overlap term in Eq. (32) it is found that it is identical to the results given by Levine.[4] This is expected, since in the present approximation the molecular overlap term is independent of molecular orientations and hence is formally the same as the rare-gas case. Examining this term further it is found that the peak ω_o in spectrum is given by $\omega_o \simeq 6\kappa T[(1+\delta)^{\frac{1}{2}}-1]^{-1}$ where $\delta = 4m\kappa T/\gamma^2$. For low temperatures ($\kappa T \ll \kappa T_o = \gamma^2/4m$) α is independent of temperature, while for high temperatures ($\kappa T \gg \kappa T_o = \gamma^2/4m$) $\alpha \sim (\kappa T)^{\frac{1}{2}} \exp[-(\omega m^{\frac{1}{2}}/\gamma(\kappa T)^{\frac{1}{2}})]$. The values of κT_o for the systems considered here are 100 cm^{-1}, 40 cm^{-1}, and ~ 6 cm^{-1} for H_2-He, H_2-Ar, and N_2-Ar respectively. Room temperature ($\kappa T \simeq 200$ cm^{-1}) lies in the high temperature region for the cases considered here. Also, the temperature dependence of the location of the peak in the absorption spectrum is given by ($\kappa T \ll \kappa T_o$) $\omega_o \sim$ constant independent of temperature for low temperatures, and ($\kappa T \gg \kappa T_o$)$\omega_o \sim (\kappa T)^{\frac{1}{2}}$ for high temperatures. That is, for low temperatures the peak in the spectrum remains fixed as the

temperature is varied, while for high temperature the peak moves toward higher wave numbers as the temperature is increased (and vice versa).

The width of the absorption spectrum $\Delta\omega$ is approximately $6\kappa T[(1 + T/T_0)^{\frac{1}{2}} - 1]^{-1}$. For low temperatures ($T \ll T_0$), $\Delta\omega \sim 12\kappa T_0$ (i.e., independent of temperature), while for high temperatures ($T \gg T_0$), $\Delta\omega \sim 6(\kappa T_0)^{\frac{1}{2}} (\kappa T)^{\frac{1}{2}}$ (i.e., proportional to the square root of the temperature). These two limiting cases may also be obtained directly from physical arguments. The low temperature case, $T \ll T_0$, implies $P \ll \gamma$ where P is the relative momentum of the colliding particles. The induced moment gives rise to an attractive force which increases the relative kinetic energy from a very small value ($P^2/2m$) at large distances to a value $\Delta E \sim \gamma^2/2m$ at distances of the order γ^{-1}. From the uncertainty principle ($\Delta E \Delta t \sim 1$), the transition rate ($\sim \Delta t^{-1}$) and hence the width of the spectrum is $\Delta\omega = 2\pi\Delta E = \Delta t^{-1} \sim \pi\gamma^2/m = 4\pi\kappa T_0$ (i.e., independent of temperature). For the high temperature case, $T \gg T_0$, we have $\Delta\omega \sim 2\pi\Delta t^{-1}$. In this case the rate is approximately $(\kappa T/m)^{\frac{1}{2}}$ and the distance approximately γ^{-1} (as can be inferred from the uncertainty principle). Therefore, $\Delta\omega \sim 4\pi(\kappa T)^{\frac{1}{2}} (\kappa T_0)^{\frac{1}{2}}$.

Numerical estimates of the overlap-induced dipole parameters in H_2, N_2/rare-gas atom systems and quantitative results for the absorption coefficients for these cases are given in the next section.

IV. ABSORPTION SPECTRUM OF H_2-RARE ATOM AND N_2-Ar MIXTURES

OVERLAP DIPOLE PARAMETERS FOR DIATOMIC MOLECULE/RARE-GAS MIXTURES

In order to obtain numerical results, estimates of the phenome-
nological parameters μ_o and γ are required. Levine and Birnbaum[3,4]
have determined these parameters for three cases of rare-gas atoms;
values are given in the following table.

DIPOLE PARAMETERS FOR RARE-GAS MIXTURES

Parameter	System		
	He-Ne	He-Ar	Ne-Ar
$\gamma(\text{\AA}^{o-1})$	1.920	1.357	1.446
μ_o(debyes)	0.121	0.166	0.223

In order to estimate μ_o and γ for systems considered here it is
assumed that γ^{-1} is proportional to the collision diameter σ occurring
in the interparticle potential and that μ_o is proportional to both
the collision diameter and the number of electrons in the outer shells
of the component particles. The first assumption seems reasonable,
since the range of the induced moment is proportional to the separation
of the particles when their electron clouds are overlapping and hence
to the collision diameter characteristic of the interparticle potential.
The second assumption also seems reasonable since the magnitude of the
dipole moment is proportional to the mean separation of charges (which
is taken to be γ^{-1}) and the mean number of electrons involved in the

collision (taken as the electrons in the outer shells of the colliding particles).[*] The inner electrons are too closely bound to be of much consequence to the induced moment.

Hence,

$$\frac{\mu_o}{N\sigma} = \text{constant} \tag{33a}$$

and

$$\gamma\sigma = \text{constant} \tag{33b}$$

where σ is the collision diameter and N is the number of electrons in the outer shells of the colliding particles. From the values given in the Table, for example, Eq. (33a) is fairly well satisfied. From Eqs. (33a) and (33b)

$$\frac{\mu_{o_A}}{\mu_{o_B}} = \frac{(N\sigma)_A}{(N\sigma)_B} = \frac{(N\gamma^{-1})_A}{(N\gamma^{-1})_B} \tag{34}$$

where the subscripts refer to two different mixtures. For the three cases given in the Table:

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[*]Since the induced dipole moment is taken as a superposition of two terms (the rare-gas atom interacting with each of the two atomic components of the molecule respectively) the molecular electron contribution to N is taken as one half of the number of outer shell molecular electrons while all of the outer shell electrons in t rare-gas atom are counted.

1) A = He-Ne   B = He-Ar

$$\frac{\mu_{o_A}}{\mu_{o_B}} = 0.73 \qquad\qquad \frac{(N\gamma^{-1})_A}{(N\gamma^{-1})_B} = 0.71$$

2) A = He-Ne   B = Ne-Ar

$$\frac{\mu_{o_A}}{\mu_{o_B}} = 0.54 \qquad\qquad \frac{(N\gamma^{-1})_A}{(N\gamma^{-1})_B} = 0.47$$

3) A = He-Ar   B = Ne-Ar

$$\frac{\mu_{o_A}}{\mu_{o_B}} = 0.74 \qquad\qquad \frac{(N\gamma^{-1})_A}{(N\gamma^{-1})_B} = 0.68$$

The ratios agree fairly well for these cases.

Values of γ and μ_o for H_2-He, H_2-Ar and N_2-Ar systems are now estimated. Equation (33b) implies $\gamma_A/\gamma_B = \sigma_B/\sigma_A$. Then

$$\gamma_{H_2\text{-He}} = (\gamma_{He\text{-Ar}})\ \sigma_{He\text{-Ar}}/\sigma_{H_2\text{-He}}$$

$$\cong 1.6\ \overset{o}{A}{}^{-1} \tag{35a}$$

$$\gamma_{H_2\text{-Ar}} = (\gamma_{He\text{-Ar}})\ \sigma_{He\text{-Ar}}/\sigma_{H_2\text{-Ar}} = 1.2\ \overset{o}{A}{}^{-1} \tag{35b}$$

and

$$\gamma_{N_2\text{-Ar}} = (\gamma_{He\text{-Ar}})\ \sigma_{He\text{-Ar}}/\sigma_{N_2\text{-Ar}} = 1.1\ \overset{o}{A}{}^{-1} \tag{35c}$$

to two significant figures. In arriving at these results the value of the collision diameter σ was obtained in the usual way as the arithmetic mean of the values for the component gases.[10] $(\sigma_{H_2-He} = 2.46 \text{ Å}, \sigma_{H_2-Ar} = 3.19 \text{ Å}, \sigma_{N_2-Ar} = 3.7 \text{ Å}, \text{ and } \sigma_{He-Ar} = 2.91 \text{ Å}.)$ From Eq. (34),

$$(\mu_o)_{H_2-He} \cong \frac{(N\gamma^{-1})_{H_2-He}}{(N\gamma^{-1})_{He-Ar}} (\mu_o)_{He-Ar} = 0.044 \text{ debyes} \tag{36a}$$

$$(\mu_o)_{H_2-Ar} \cong \frac{(N\gamma^{-1})_{H_2-Ar}}{(N\gamma^{-1})_{He-Ar}} (\mu_o)_{He-Ar} = 0.16 \text{ debyes} \tag{36b}$$

and

$$(\mu_o)_{N_2-Ar} \cong \frac{(N\gamma^{-1})_{N_2-Ar}}{(N\gamma^{-1})_{He-Ar}} (\mu_o)_{He-Ar} = 0.27 \text{ debyes} \tag{36c}$$

The quantitative results for the absorption spectrum follow.

ABSORPTION SPECTRUM FOR H_2/RARE-GAS ATOM

First consider the H_2-He system. The reduced mass m for H_2-He is approximately 4/3 amu (atomic mass unit) and the rotational constant B for H_2 is 59.3 cm^{-1}.[6] In this example and the following the tempera- ture T is taken to be of the order of room temperature (i.e., $\varkappa T \simeq 200 \text{ cm}^{-1}$). Using these values for B and $\varkappa T$ it is easy to see that only the ground and first few (about three) excited rotational states of H_2 are appreci- ably excited under equilibrium conditions. The nuclear spin of H_2 is $\frac{1}{2}$, hence the total wave function must be antisymmetrical. This implies

that the relative nuclear statistical weights are 1 and 3 for even
and odd rotational states respectively. The polarizability of He is
$\cong 0.21 \times 10^{-24} cm^3$ (Ref. 11) and the quadrupole moment of H_2 is
$\cong 0.49 ea_o^2$ (Ref. 7) where e is the electron charge and a_o is the Bohr
radius. Substituting numerical values in Eq. (32) gives (at
$\kappa T \cong 200 cm^{-1}$)

$$\alpha_{H_2-He}(k) \cong 1.53 \times 10^{-46} \left[Q + \sum_{J=0}^{3} S(J) \right] n_1 n_2 (cm^{-1}) \qquad (37)^*$$

where Q is the sum given in Eq. (32) with $J_i = J_f$, $J_i = 0,1,2,3$, S(J)
is given by the summand in Eq. (32) with $J \equiv J_i$, $J_f = J_i - 2$, and
the wave number is k cm^{-1}. In Fig. 1 the contributions of the
various branches and the sum of these branches are plotted as a function
of the wave number k (i.e., $k = \omega/2\pi$). The Q branch contains contribu-
tion from both the overlap and quadrupole-induced dipole moments (the
overlap term being ~ 90 percent of the Q branch contribution), while
only the quadrupole-induced moment contributes to S branches.[**]

As another example the H_2-Ar system is considered. The reduced
mass H_2-Ar is approximately 1.91 amu, and the polarizability of Ar is
$\sim 1.63 \times 10^{-24} cm^3$ (Ref. 12). Substituting numerical values into
Eq. (32) gives (at $\kappa T \sim 200 cm^{-1}$)

---

[*]In all cases discussed here the contribution to α from the O
branches was found to be negligible compared to the contributions
from the Q and S branches.

[**]At $\omega = E_{J_f J_i}$ (resonance) Eq. (32) indicates that the quadrupole
contribution becomes very large. $I_q \sim \log (\omega - E_{J_f J_i})$. Strictly speaking,
the rotational transition lines are not infinitely short but have very
narrow pressure broadened lines ($\ll 1 cm^{-1}$) at room temperature and
atmospheric pressure. The absorption at resonance is finite; $I_q \sim \log$
$[(\omega - E_{J_f J_i})^2 + \gamma^2/4]$ where γ is the half width of the line. Due to the lack
of knowledge of these line widths, the increase in the absorption spectrum
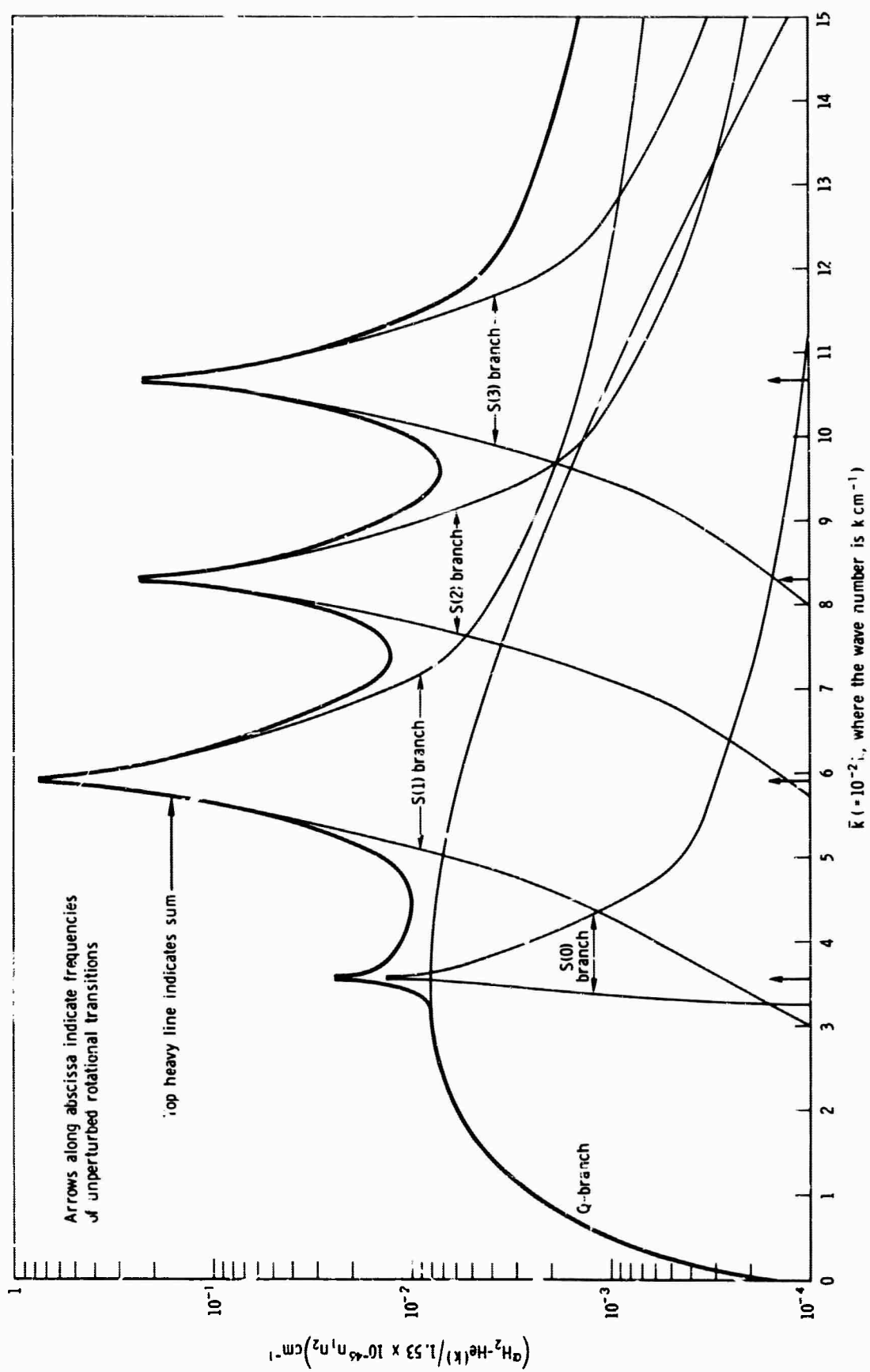very near a resonance is indicated schematically.

Fig. 1—Absorption coefficient for H_2-He system at room temperature with contributions of Q and S branches indicated

$$\alpha_{H_2\text{-}Ar}(k) \cong 3.75 \times 10^{-46} \left[Q + \sum_{J=0}^{3} S(J) \right] n_1 n_2 (cm^{-1}) \qquad (38)$$

In Fig. 2 the contribution of the various branches and the sum of these branches are plotted as a function of wave number. In this case the absorption coefficient is roughly an order of magnitude larger than the H_2-He case. This is due mainly to the larger reduced mass of the H_2-Ar system and the larger polarizability and induced moment of Ar and H_2-Ar system as compared with H_2-He.

ABSORPTION SPECTRUM FOR N_2-Ar

Due to the relatively large rotational constant of H_2 ($B_o = 59.3$ cm^{-1}), the absorption spectrum, at room temperature, can be resolved into two parts; a pure translational component (Q branch), and a rotation-translation component (S branch). On the other hand, in the case of N_2 the rotational constant is much smaller than for H_2 ($B_{N_2} \cong 2$ cm^{-1}), with the result that at room temperature the Q and S branches completely overlap. That is, a resolution of the absorption spectrum of N_2/rare-gas atom systems into a translational component and a rotation-translation component is not possible. The N_2-Ar system is considered. The reduced mass of N_2-Ar is approximately 10.4 amu, the quadrupole moment of N_2 is $\simeq 1.1$ ea$_o^2$ (Ref. 13). The nuclear spin of N_2 is 1, which implies that the relative nuclear statistical weights are 2 and 1 for even and odd rotational states respectively. At room temperature it is necessary to include the ground and about the first twenty excited rotational states in the statistical average. Substituting numerical values into Eq. (32) gives ($\kappa T \simeq 200$ cm^{-1})
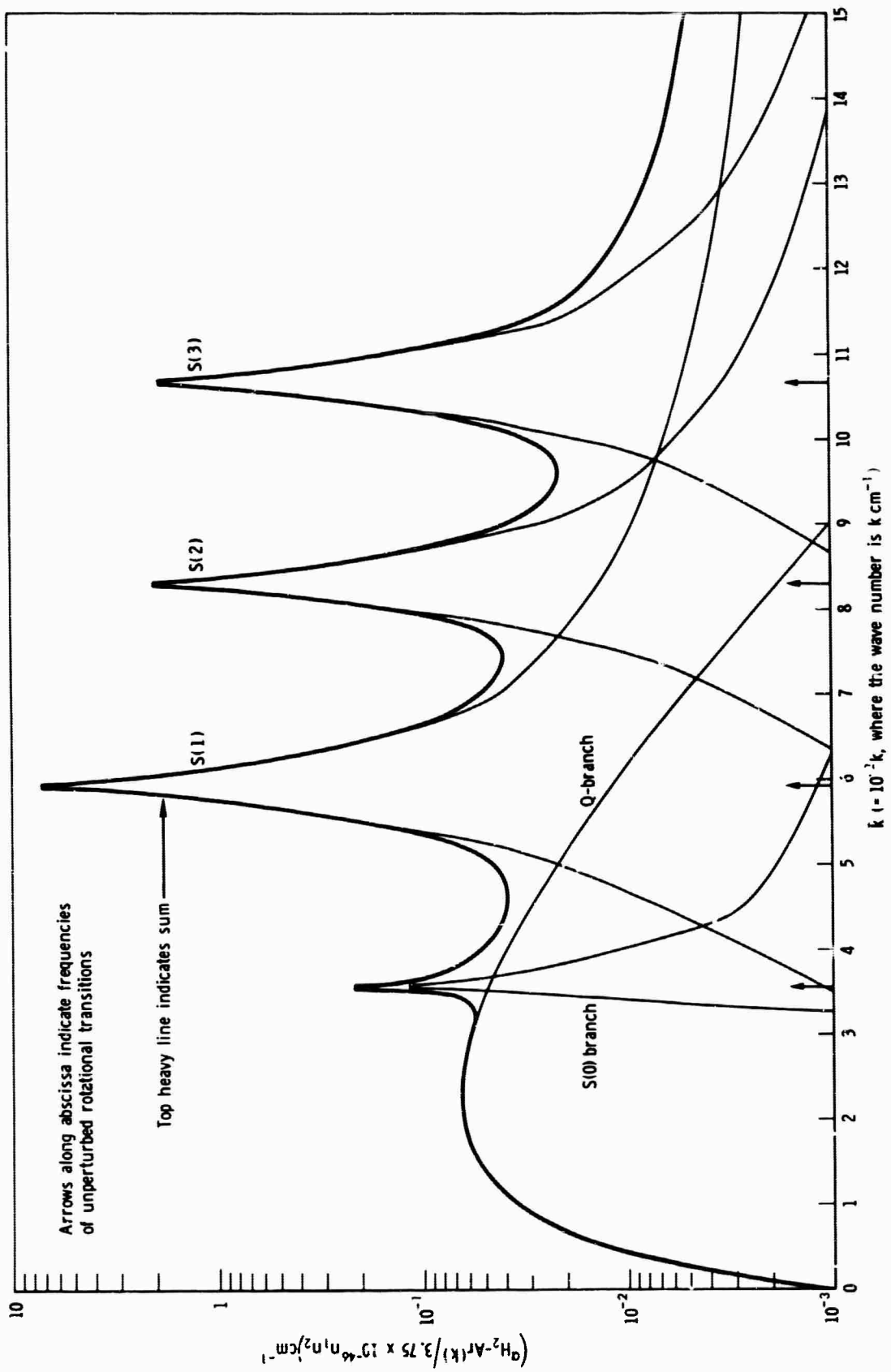
Fig. 2—Absorption coefficient for H_2-Ar system at room temperature with contributions of Q and S branches indicated

$$\alpha_{N_2-Ar}(k) \simeq 2.6 \times 10^{-47} R(k) \, n_1 n_2 (cm^{-1}) \qquad (39)$$

where $R(k) = Q + \sum_{j=0}^{20} S(J)$. The absorption coefficient for N_2-Ar
is plotted in Fig. 3 (the S branch contributes about 90 percent
of the total to $R(k)$). Very close ($<< 1 \, cm^{-1}$) to a transition
line the absorption becomes large, but this occurs in a very
narrow region about each line (compared to the spacing between them).
Due to lack of knowledge of the relevant line widths, the curve
shown in Fig. 3 is the envelope of points away from rotational transi-
tion lines. Very close to the resonances the absorption spectrum
has a series of very narrow spikes. The contribution of these resonance
lines to the integrated absorption coefficient is negligible, since
these lines are so narrow; therefore they are not indicated in Fig. 3.

From the N_2-Ar spectrum an estimate of the absorption in N_2-N_2
that involves single rotational transitions may be easily obtained.
Single (as opposed to double) rotational transitions are those
which involve a rotational transition in one of the colliding mole-
cules but not in both. To obtain this, one substitutes the polariz-
ability, reduced mass, the collision diameter for the N_2-N_2 system,
and an overall factor of two for that of the N_2-Ar system. This
method treats one of the N_2 modules essentially as a rare-gas atom--
that is, as having no internal energy levels to excite it. It is
found that at the peak of the spectrum ($\sim 100 \, cm^{-1}$, room temperature
and atmospheric pressure) the absorption coefficient is of the
order of $0.8 \times 10^{-6} \, cm^{-1}$. Bosomworth and Gush[2] report an experi-
mental absorption coefficient of $\sim 4 \times 10^{-6} \, cm^{-1}$ at $\sim 100 \, cm^{-1}$.
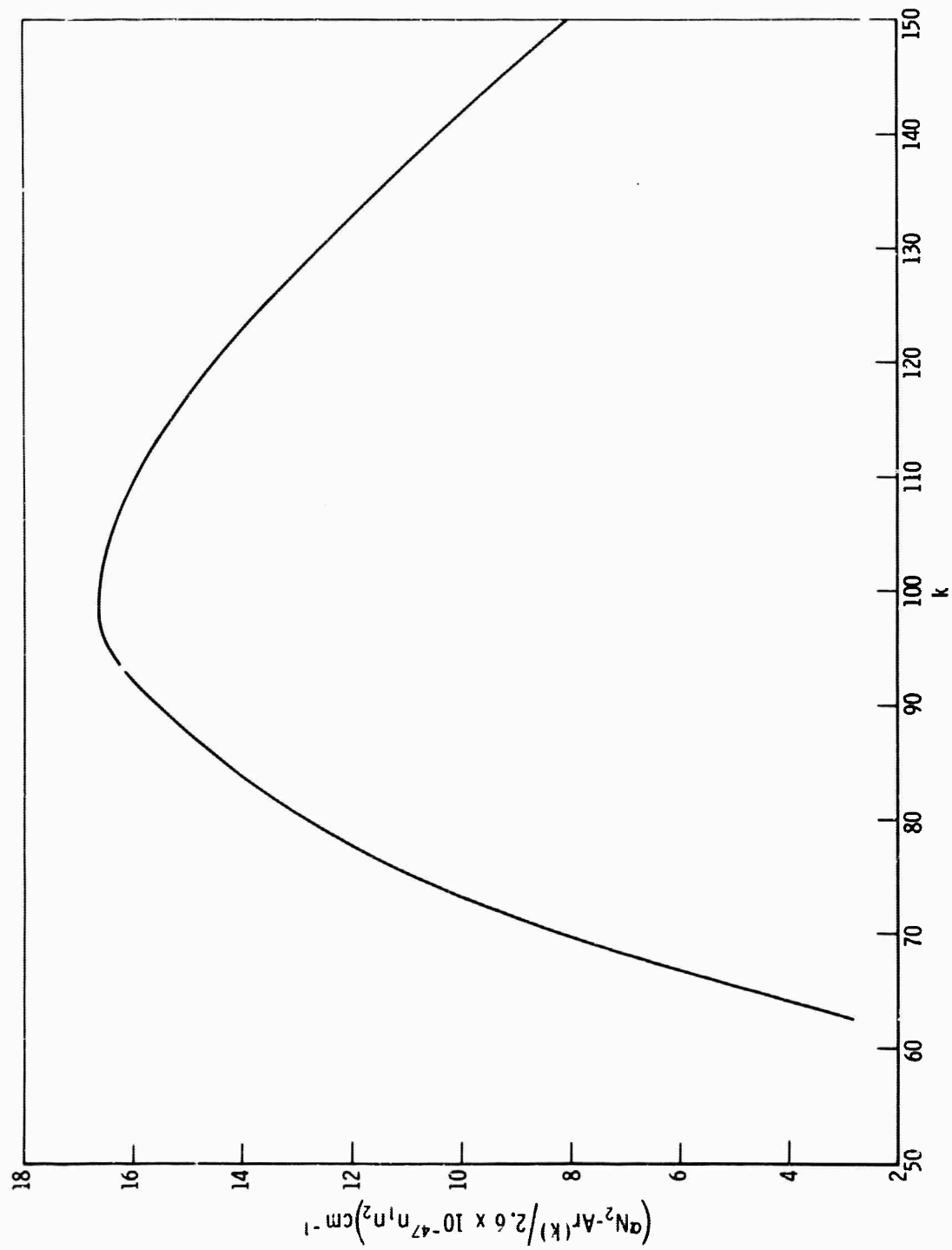Presumably the reason for this discrepancy of values lies,

Fig. 3—Absorption coefficient for N_2-Ar system at room temperature

in part, in the failure of our analysis to include the contribution of double rotational transitions.

ESTIMATES FOR N_2-N_2 ABSORPTION IN THE FAR WINGS

For frequencies $\omega \gg \kappa T$ and $E_{J_f J_i}$ the momentum transfer Q becomes large (Qa $\gg$ 1 where a is one-half the internuclear spacing $\cong 0.5$ $\overset{o}{A}$ for N_2). This can be seen as follows: $Q = |\vec{k}'-\vec{k}|$ and $k'^2/2m = k^2/2m + \omega - E_{J_f J_i}$; $k^2/2m \sim \kappa T$, hence for $\omega \gg \kappa T$, $E_{J_f J_i}$ implies $Q \sim (2m\omega)^{\frac{1}{2}}$. Thus for large ω, $Q \sim \omega^{\frac{1}{2}}$. At the CO_2 laser wavelength ($k \cong 10^3 cm^{-1}$) we find $Qa \gtrsim 1$, and hence the overlap moment is angle-dependent (i.e., $e^{i\vec{Q}\cdot\vec{a}} \neq 1$). Large Q implies close collisions and hence the quadrupole-induced moments do not contribute. Also, since the overlap moment is angle-dependent the N_2-N_2 system no longer possesses a center of symmetry and can have a nonzero overlap-induced dipole moment. By a process similar to that which led to Eqs. (35) and (36), it is found that ($\sigma_{N_2-N_2} = 3.75$ $\overset{o}{A}$)

$$\gamma_{N_2-N_2} = (\gamma_{He-Ar}) \, \sigma_{He-Ar}/\sigma_{N_2-N_2} = 1.05 \, \overset{o}{A}^{-1} \tag{40}$$

and

$$(\mu_o)_{N_2-N_2} = \frac{(N\gamma^{-1})_{N_2-N_2}}{(N\gamma^{-1})_{He-Ar}} (\mu_o)_{He-Ar} = 0.11 \text{ debyes} \tag{41}$$

Instead of using Eq. (12), we take the overlap-induced dipole moment of the two molecule system to be

$$\vec{\mu}(r) = \vec{\mu}(r_1) + \vec{\mu}(r_1') + \vec{\mu}(r_2) + \vec{\mu}(r_2') \tag{42}$$

The vectors $\vec{r}_1$, $\vec{r}_1{}'$, $\vec{r}_2$, and $\vec{r}_2{}'$ are defined in Fig. 4. Letting $\vec{r}$ be the vector between the centers of mass of the two molecules, and calling the molecular internuclear separation vector $2\vec{a}_1$ and $2\vec{a}_2$, where the subscripts 1 and 2 refer to the two molecules respectively, it is seen that

$$
\left.
\begin{aligned}
\vec{r} - \vec{a}_2 - \vec{r}_2 - \vec{a}_1 &= 0 \\[6pt]
\vec{r} + \vec{a}_2 - \vec{r}_1 - \vec{a}_1 &= 0 \\[6pt]
\vec{r} - \vec{a}_2 - \vec{r}_2{}' + \vec{a}_1 &= 0 \\[6pt]
\vec{r} + \vec{a}_2 - \vec{r}_1{}' + \vec{a}_1 &= 0
\end{aligned}
\right\}
\tag{43}
$$

The integral over the relative coordinate $(\vec{r})$ is the same as before, that is, in place of Eq. (17), it can be shown that

$$
H \equiv \left\langle (JM)_f^{(1)}(JM)_f^{(2)} \,|\, \mu_z \,|\, (JM)_i^{(1)}(JM)_i^{(2)} \right\rangle = A_o Q_z \left[\left\langle f \,|\, e^{i\vec{Q}\cdot\vec{a}_1} \,|\, i \right\rangle_{(1)} \right.
$$

$$
\times \left\langle f \,|\, e^{i\vec{Q}\cdot\vec{a}_2} \,|\, i \right\rangle_{(2)} + \left\langle f \,|\, e^{i\vec{Q}\cdot\vec{a}_1} \,|\, i \right\rangle_{(1)} \left\langle f \,|\, e^{-i\vec{Q}\cdot\vec{a}_2} \,|\, i \right\rangle_{(2)}
$$

$$
\left. + \text{ terms } a_1 \to -a_1, \; a_2 \to -a_2 \right]
\tag{44}
$$

where the sub- and superscripts 1 and 2 refer to each of the two molecules respectively and

$$
A_o = \frac{\mu_o \pi^{3/2}}{2} \gamma^{-4} e^{-(Q^2/4\gamma^2)}
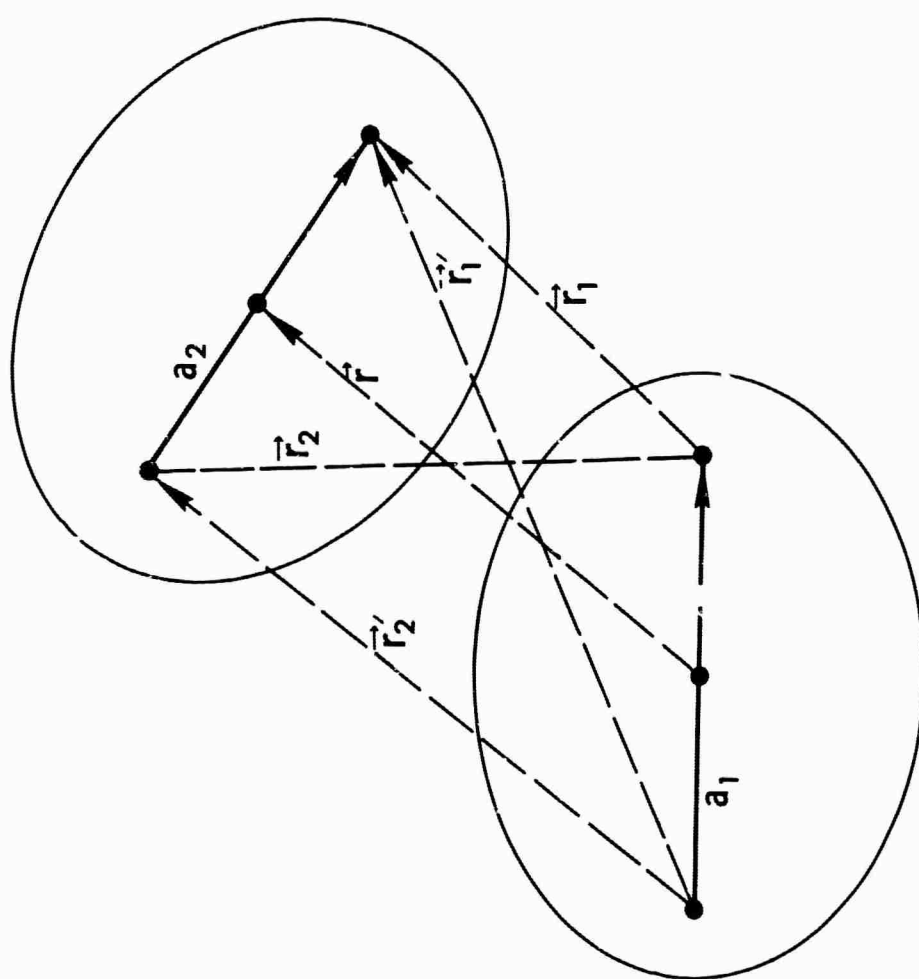\tag{45}
$$

Fig. 4—Geometrical relationship for binary molecular collisions

Taking the z-axis parallel to the polarization vector of the photon, we expand $e^{i\vec{Q}\cdot\vec{a}}$ in terms of spherical harmonics; that is,

$$e^{i\vec{Q}\cdot\vec{a}} = 4\pi \sum_{J=0}^{\infty} i^J j_J(Qa) \sum_{M=-J}^{+J} Y_{JM}(\Omega_a) Y_{JM}^*(\Omega_Q) \tag{46}$$

where Y_{JM} are spherical harmonics, and Ω_a and Ω_Q are the angular coordinates of the vectors $\vec{a}$ and $\vec{Q}$ respectively. Because of the symmetry of the N_2 molecule about its center of mass, only even J's will contribute (as can be deduced from Eq. (44)).[*] Also, since $Qa \gtrsim 1$ the asymptotic form of the spherical Bessel function is used:

$j_J(Qa) \sim \sin(Qa - \frac{J\pi}{2})/Qa = (-1)^{J/2} \sin Qa/Qa$ for even J.

The average over the azimuthal quantum numbers takes the form

$$\overline{H^2} \equiv (2J_{i}+1)_{(1)}^{-1} (2J_{i}+1)_{(2)}^{-1} \sum_{(M_i)_1 (M_i)_2 (M_f)_1 (M_f)_2} H^* H \tag{47}$$

Substituting Eq. (46) into Eq. (44) and obtaining the indicated rotational matrix elements (which can be expressed in terms of Clebsch-Gordan coefficients), the operations indicated in Eq. (47) are then performed. The sums over the M values can be obtained by using the orthogonality conditions on the Clebsch-Gordan coefficients, and it is found that

$$\overline{H^2} = 16Q_z^2 \left[\frac{\sin Qa_1}{Qa_1}\right]^2 \left[\frac{\sin Qa_2}{Qa_2}\right]^2 F_{(i,f)}^{(1)} F_{(i,f)}^{(2)} \tag{48}$$

---

[*] Since J is even, it can be deduced that $J_i + J_f$ must be even.

where

$$F(i,f) = \left(\frac{2J_i+1}{2J_f+1}\right) \sum_{J(even)} (2J+1)^2 \, C^2(J_i,J,J_f,00) \tag{49}$$

In the following, $a_1 = a_2 = a$. Replacing Eq. (30), it is found that

$$\alpha(\omega) \sim (2\pi)^{-4}(4m/3\epsilon a^4) \int_0^\infty \frac{dQ}{Q} \sin^4 Qa \; e^{-\epsilon k_Q^2} e^{-Q^2/2\gamma^2}$$

$$= (2\pi)^{-4}(4m/6\epsilon a^4) \; e^{\epsilon\Delta^2/2} \int_0^\infty \frac{d(Q^2)}{Q^2} \sin^4 Qa$$

$$\times \exp\left[-Q^2(\frac{1}{2\gamma^2} + \frac{\epsilon}{4}) - \frac{\epsilon\Delta^4}{4Q^2}\right]$$

$$= (2\pi)^{-4}(4m/6\epsilon a^4) \; e^{\epsilon\Delta^2/2} \; I_1(\omega)$$

where

$$I_1(\omega) = \int_0^\infty \frac{dx}{x} \; e^{-[x(A+B) + \frac{B}{x}]} \sin^4 Cx^{\frac{1}{2}}$$

and

$$A = \Delta^2/2\gamma^2 = m\omega/\gamma^2$$

$$B = \epsilon\Delta^2/4 = \omega/4\kappa T$$

$$C = \Delta a = (2m\omega)^{\frac{1}{2}}a$$

$$\left.\begin{array}{l} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array}\right\} \tag{50}$$

For $\omega \sim CO_2$ laser frequency, $C > 1$ and hence the $\sin^4$ term in the integrand of I_1 oscillates rapidly over the region where the exponential is nonzero. Hence, its average value may be used, yielding

$$I_1 \cong \frac{3}{8} \int_0^\infty \frac{dx}{x} \; e^{-[(A+B)x + \frac{B}{x}]}$$

$$= \frac{3}{4} \left(\frac{1}{1+\delta}\right) K_0(2B \sqrt{1+\delta})$$

where (51)

$$\delta = B/A = 4m\varkappa T/\gamma^2$$

Hence it is found for $\omega \gg \varkappa T$, $E_{J_f J_i}$ that

$$\alpha_{N_2-N_2}(\omega) \cong \frac{(n^2/2) \; m\omega \; \mu_0^2 \; e^{\omega/2\varkappa T} \; K_0\left(\frac{\omega}{2\varkappa T}\sqrt{1 + \frac{4m\varkappa T}{\gamma^2}}\right)}{8(2\pi m\varkappa T)^{\frac{1}{2}}\gamma^8 a^4 \left(1 + \frac{4m\varkappa T}{\gamma^2}\right)}$$

$$\times \left\{ Z^{-1} \sum_{\substack{J_i=0 \\ J_f=J_i+\Delta J}}^{20} e^{-\frac{B}{\varkappa T} J_i(J_i+1)} F(i,f) g_i (2J_i+1) \right\}^2 \quad (52)$$

where

$$Z = \sum_{J_i=0}^{20} e^{-\frac{B}{\varkappa T} J_i(J_i+1)} g_i (2J_i+1)$$

$F(i,f)$ is given by Eq. (49), and the molecular density is $n \; cm^{-3}$.[*] In obtaining Eq. (52) the term $(2J_f+1)e^{-\omega/\varkappa T}$ has been dropped since $\omega \gg \varkappa T$. For N_2-N_2 systems the reduced mass is 7 amu and $a = .505 \; A^{-1}$. Hence from Eqs. (40), (41) and (52) it is found that at room temperature

---

[*]The factor $n^2/2$ appears in Eq. (52) (instead of n^2) in order to count each collision once.

$$\alpha_{N_2 - N_2}(k) \simeq 4.5 \times 10^{-42} \, n^2 \left\{ \bar{k} \, K_0(3.17\bar{k}) e^{\bar{k}/4} \right\} \ (cm^{-1}) \qquad (53)$$

$$\approx 3.2 \times 10^{-42} \, n^2 \, \bar{k}^{-\frac{1}{2}} \, e^{-2.92\bar{k}}, \ \text{for } \bar{k} \gg 1/3.17$$

where $\bar{k} = 10^{-2}k$. In obtaining these results only those final states corresponding to $\Delta J = 0, \pm 2$ have been included. Since the overlap-induced moment falls off very rapidly with increasing interparticle separation (the moment having a maximum for $r = \gamma^{-1} \lesssim$ molecular separation), angular momentum considerations imply that $\Delta J = |J_f - J_i| \lesssim 2$ for N_2. This can be seen by estimating the order of magnitude of the relative angular momentum of the colliding particles, mvr, with $v \sim (\kappa T/m)^{\frac{1}{2}} \, r \sim \gamma^{-1}$ and noting that the photon contributes one unit of angular momentum. At the CO_2 laser wave number $\bar{k} \cong 9.44$ it is found that

$$\alpha(k_{CO_2}) \cong 3.3 \times 10^{-54} n^2 \ (cm^{-1}) \qquad (54)$$

$$= 2.5 \times 10^{-15} \ cm^{-1}$$

at atmospheric pressure ($n \sim 2.7 \times 10^{19}$), which is very small. Even at high pressures the absorption coefficient remains small. For example, at 100 atmospheres the absorption coefficient at 10.6μ is $\sim 2 \times 10^{-11} \ cm^{-1}$. Finally it is noted that the absorption coefficient is relatively insensitive to temperature; therefore no large change in α is obtained by varying the temperature.

V.   CONCLUSIONS

The results obtained for N_2/rare-gas atom and N_2-N_2 absorption in the far wing were deduced from a model which assumes a specific functional form for the overlap-induced dipole moment. The dependence on interparticle separation is of the form used by Levine,[4] while the angular dependence is introduced by assuming that the total overlap moment is a superposition of one particle interacting with each of the atomic components of the molecule respectively, the latter assumption having important effects for close collision, when details of the intermolecular potential become important. For close collisions the assumption of plane waves to describe the relative translational motion of the two particles is offset by assuming that the dipole moment goes to zero for small r, i.e., $\mu = \mu_0 \gamma r e^{-\gamma^2 r^2}$. The factor γr is used to simulate the effect of the scattering wave functions. Levine[4] has shown that this model is relatively insensitive to the effects of the interparticle potential for wave numbers near the peaks in the rare-gas spectrum (100-400 cm^{-1}). No experimental results as yet exist for the far wings, and hence the accuracy of an extrapolation of the overlap model into the far wings cannot be ascertained. The results obtained here for N_2-N_2 absorption at $k \sim 1000$ cm^{-1} have been based on an extrapolation of this model. The absorption coefficient obtained is very small and it is not felt that any refinement of the model will produce orders of magnitude changes in α. Therefore it is concluded that this mechanism does not play an important role in the atmosphere for the absorption of 10.6μ radiation by nitrogen.

Appendix

EVALUATION OF $I(\omega)$

Consider the integral $I(\omega)$ defined in Eq. (28):

$$I(\omega) = \int_0^\infty dx \; e^{-Ax - \frac{B}{x}} \sin^2 Cx^{\frac{1}{2}} \tag{55}$$

A, B and C are given in Eq. (28)   At $x \to 0$ and $x \to \infty$ the integrand approaches zero exponentially and has a maximum for $x = (B/A)^{\frac{1}{2}}$. Upon examining the numerical values of parameters for the cases discussed in the text it can be seen that the $\sin^2 Cx$ term is a slowly varying function of x in the region where the exponential term is nonzero. Hence, upon substituting those values of x in which the exponential term is maximum into the $\sin^2$ term,

$$I(\omega) \simeq \sin^2[C(B/A)^{\frac{1}{2}}] \int_0^\infty dx \; e^{-Ax - \frac{B}{x}}$$

$$= - \sin^2[C(B/A)^{\frac{1}{2}}] \frac{\partial}{\partial A} \left\{ \int_0^\infty \frac{dx}{x} e^{-Ax - \frac{B}{x}} \right\} \tag{56}$$

$$= - 2 \sin^2[C(B/A)^{\frac{1}{2}}] \frac{\partial}{\partial A} \left\{ K_0[2(AB)^{\frac{1}{2}}] \right\}$$

The formula

$$\int_0^\infty \frac{dx}{x} e^{-Ax - \frac{B}{x}} = 2K_0[2(AB)^{\frac{1}{2}}]$$

has been used.[9]   It can be shown that

$$\frac{\partial K_0[2(AB)^{\frac{1}{2}}]}{\partial A} = - (B/A)^{\frac{1}{2}} K_1[2(AB)^{\frac{1}{2}}] \tag{57}$$

Hence, from Eqs. (56) and (57),

$$I(\omega) \cong 2 \sin^2[C(B/A)^{\frac{1}{2}}] (B/A)^{\frac{1}{2}} K_1[2(AB)^{\frac{1}{2}}] \tag{58}$$

REFERENCES

1. Kiss, A. J., and H. L. Welsh, <u>Phys. Rev. Letters</u>, Vol. 2, 1959, p. 166.

2. Bosomworth, D. R., and H. P. Gush, "Collision-Induced Absorption of Compressed Gases in the Far Infrared, Part II," <u>Can. J. Phys.</u>, Vol. 43, 1965, p. 729.

3. Levine, H. B., and G. Birnbaum, "Classical Theory of Collision-Induced Absorption in Rare-Gas Mixtures," <u>Phys. Rev.</u>, Vol. 154, 1967, p. 86.

4. Levine, H. B., and G. Birnbaum, "Quantum Theory of Collision-Induced Absorption in Rare-Gas Mixtures," <u>Phys. Rev.</u>, Vol. 160, 1967, p. 159.

5. Van Kranendonk, J., "Induced Infra-Red Absorption in Gases," <u>Physica</u>, Vol. 24, 1958, p. 347.

6. Herzberg, G., <u>Spectra of Diatomic Molecules</u>, D. Van Nostrand Co., Inc., New York, 1959.

.   Van Kranendonk, J., and J. D. Poll, "Theory of Translational Absorption in Gases," <u>Can. J. Phys.</u>, Vol. 39, 1961, p. 189.

8. Rose, M. E., <u>Elementary Theory of Angular Momentum</u>, John Wiley and Sons, Inc., New York, 1957.

9. Grobner, W., and N. Hofreiter, <u>Bestimmte Integrale</u>, Springer-Verlag, Berlin, 1950, p. 66.

10. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, <u>Molecular Theory of Gases and Liquids</u>, John Wiley and Sons, Inc., New York, 1964, p. 15.

11. Johnston, D. R., G. J. Oudemans, and R. H. Cole, "Dielectric Constants of Imperfect Gases," <u>J. Chem. Phys.</u>, Vol. 33, 1960, p. 1310.

12. Bornstein, L., <u>Zahlenwerte und Funktionen</u>, Vol. 1, Part 1, Springer-Verlag, Berlin, 1950.

13. Townes, C. H., and A. L. Schawlow, <u>Microwave Spectroscopy</u>, McGraw-Hill Book Company, Inc., New York, 1955, p. 365.

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A quantum mechanical calculation is given for collision-induced absorption in the infrared and far-infrared spectral regions for mixtures consisting of symmetrical diatomic molecules and rare-gas atoms. The induced moment consists of a short-range overlap term and a long-range quadrupole term. Near molecular transition lines, the quadrupole term gives the main contribution to the absorption, while in the far wings, the overlap term is dominant. The Hydrogen(sub 2)-Helium, Hydrogen(sub 2)-Argon, and Nitrogen(sub 2)-Argon systems are considered, and an estimate is given of the absorption coefficient near 10 millimicrons for Nitrogen(sub 2)-Nitrogen(sub 2) systems.	Lasers Electronics Physics Gas dynamics H_2-H_2, H_2-A, N_2-A N_2-N_2